

SOME ADDITION REACTIONS OF
1-CYANO-1,3-BUTADIENE

BY

KAZUO HORACE TAKEMURA

B.S., University of California, Los Angeles, 1947

M.S., University of Illinois, 1948

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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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INTRODUCTION

The recent development of preparative methods for 1-cyano-1,3-butadiene makes it a readily available reagent. It may be regarded as the higher vinylog of acrylonitrile, and as such it would be expected to undergo reactions, similar to the well known cyanoethylation (1) processes, with various compounds containing active hydrogen atoms. The successful development of such addition reactions would permit the introduction of a straight-chain, five-carbon fragment into organic molecules. The present work was undertaken to test the value of 1-cyano-1,3-butadiene as a reagent in organic synthesis. The compound is ordinarily obtained as a mixture of *cis*- and *trans*- isomers, which can be separated and which differ in reactivity toward Diels-Alder reagents (2). It was therefore desirable to study the pure isomers in reactions with active hydrogen compounds also, since it is conceivable that the two isomers might differ in reactivity or lead to different products.

DISCUSSION OF RESULTS

Ethyl acetoacetate (3), 2-nitropropane (4) and thiophenol were added to the pure *cis*- and *trans*-isomers of 1-cyano-1,3-butadiene. It was found that on the basis of yield of product there is little difference in the reactivities of the two isomers in addition reactions of this type. Physical properties of the products showed that the cyanobutadiene isomers yielded identical adducts.

The thiophenol adduct was proved to be a 1,6-addition product by ozonization. The isolation of β -phenylsulfonylpropionic acid (identified as the *p*-bromophenacyl ester) indicated that the adduct was phenyl 4-(1-cyano-1-butenyl) sulfide, and therefore that the olefinic double bond had migrated from the

β,γ - to the α,β -position.

Thiophenol did not add to cyanobutadiene under the influence of ultraviolet light. Benzyl mercaptan and thio- β -naphthol formed addition products in the presence of base. The reaction of thio- β -naphthol was proved to be the reaction of the sulfhydryl group with the diene, and not a cyanoalkylation of the naphthalene nucleus, by hydrogenolysis of the product to give naphthalene.

Benzylamine and cyclohexylamine added to cyanobutadiene at room temperature without a catalyst. β -Naphthylamine failed to react on heating in the presence of glacial acetic acid or potassium hydroxide. Hydroxylamine hydrochloride also failed to add.

Phenol and cyanobutadiene formed the simple ether on heating in the presence of Triton B. Similar reactions with resorcinol, catechol and phloroglucinol were unsuccessful.

β -Naphthol in the presence of a molar equivalent of potassium hydroxide gave a 1 to 1 adduct with cyanobutadiene. The same product was obtained although in poorer yields when a catalytic amount of potassium hydroxide or Triton B was used. The structure of the product was not established. Chemical evidence and infrared analysis indicated that the adduct was a cyclic ether. The behavior of the compound toward potassium permanganate, hydriodic acid and hydrobromic acid in glacial acetic acid makes it likely that it is 2,3-dihydro-1-naphtho-(2,1-b)-pyran-3-acetonitrile. Attempts to identify the compound by decarboxylation of the acid derivative to the known 3-methyl-2,3-dihydro-1-naphtho-(2,1-b)-pyran were unsuccessful.

p-Nitrobenzenediazonium chloride and cyanobutadiene reacted to give an oil which could not be purified. By treating this oil with methanolic potassium hydroxide, two products, both having the composition of a *p*-nitrophenylecyanobutadiene, were obtained in poor yields. These two products are presumed to be *cis*, *trans*-isomers. The structure of the products

were not conclusively proven. Oxidation of the intermediate oily product with aqueous potassium permanganate or ozone gave *p*-nitrobenzoic acid. The reaction probably proceeded by the attack of the *p*-nitrophenyl free radical at the α -position (5) of cyanobutadiene, with subsequent formation of 4-chloro-1-(*p*-nitrophenyl)-1-cyano-2-butene. This on treatment with methanolic potassium hydroxide gave 1-(*p*-nitrophenyl)-1-cyano-1,3-butadiene. The isolation of *p*-nitrobenzoic acid in the oxidation reactions was due presumably to the presence of small amounts of the *p*-nitrophenylcyanobutadiene in the oily intermediate product.

Cyanobutadiene failed to give addition products with *p*-aminobenzenesulfonamide, benzenesulfonanilide and phthalimide. Fluorene, benzyl phenyl sulfone and diisopropyl ketone did not react. The addition of hydrogen cyanide did not take place when cyanobutadiene was treated with aqueous potassium cyanide. Methylmagnesium iodide and cyanobutadiene gave polymeric material.

Attempts to introduce the five-carbon chain of the biotin molecule by the reaction of *dl*-4-benzamido-3-ketotetrahydro-2-thiophenecarboxylic acid methyl ester and cyanobutadiene in the presence of base were unsuccessful. The products were thick, viscous oils which could not be purified. The melting point of the keto-ester obtained in this work was different from that reported (6) but had the correct composition. The difference was assumed to be due to the presence of a mixture of stereoisomers. 4-Benzamido-3-ketotetrahydrothiophene also gave no addition product.

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VITA

The author was born on November 2, 1921, in San Juan Bautista, California. He attended the public schools of Los Angeles, California, graduating from Lincoln High School in June, 1939. He entered the University of California at Los Angeles in September, 1939, and was there until March, 1942. From February to July, 1944, he attended the University of Cincinnati in Ohio. He served in the United States Army during the period of October, 1944, to June, 1946. Upon his discharge from the Army, he returned to the University of California in August, 1946, and was awarded the degree of Bachelor of Science in August, 1947. In October of that year, he entered the Graduate College of the University of Illinois. He received the degree of Master of Science in August, 1948. He held University Fellowships during February to June, 1949, and September, 1949, to June, 1950.

